

The University of Chicago

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A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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W. G. ALSOP

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THE HYDROLYSIS OF CARBON TETRAIODIDE

W. G. ALSOP

INTRODUCTION

Several investigators¹ have reported that carbon tetraiodide yields iodoform and a hypoiodite when treated with alkaline reagents. In spite of the fact that contradictory results are recorded by other investigators, the belief that in carbon tetraiodide one atom of iodine is "positive" is quite widespread among chemists. Waters and Lowry² have even suggested the term "inverse substitution" to account for this phenomenon.

From the standpoint of the hypothesis developed by Kharasch and collaborators, it appeared highly improbable that carbon tetraiodide should yield iodoform and a hypoiodite when treated with an alkali. The recent investigation has confirmed my *a priori* conviction that "positive" iodine is not eliminated in the hydrolysis of carbon tetraiodide. Furthermore, in view of my findings, and because of the claim that "iodine is even more easily [than bromine] expelled as a positive radical by inverse substitution,"² I am inclined to believe that no methane halogen compound eliminates a "positive" halogen upon hydrolysis with alkali. The quotation from Waters and Lowry,² in support of the hypothesis of "inverse substitution" that "the ease with which iodine can be expelled is indeed so great that it can be eliminated in an elementary form from the tetrahalogen derivatives without the intervention of alkali," is without foundation, and is based upon erroneous interpretations by the original investigators. I have shown quite conclusively that the elimination of iodine from carbon tetraiodide (in benzene or chloroform) at ordinary temperatures is caused by oxygen of the air.

PREVIOUS WORK

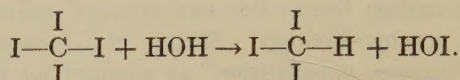
Most of the work on the interaction of carbon tetraiodide with various reagents is quite old. As early as 1874, Gustavson³ reported the forma-

¹ NEF, *Ann.*, **308**, 330 (1889); JONES, see STIEGLITZ, *J. Am. Chem. Soc.*, **44**, 1307 (1922).

² WATERS AND LOWRY, "Physical Aspects of Organic Chemistry," D. Van Nostrand Company, Inc., New York, 1936, p. 223.

³ GUSTAVSON, *Ann.*, **172**, 173 (1874).

tion of iodoform when carbon tetraiodide was heated in water solution. On the other hand, Moissan⁴ was unable to obtain any iodoform by heating carbon tetraiodide with water in a sealed, evacuated tube. The statement is made that the solution possessed no oxidizing properties. Nef,¹ however, claims that iodoform was obtained as a result of the hydrolysis of carbon tetraiodide with alcoholic potassium hydroxide, sodium ethylate, alcoholic potassium cyanide, and with alcohol alone at 100°. The details of the experimental procedure are entirely lacking. Jones¹ claims that treatment of carbon tetraiodide with water produces hypoiodous acid. If the formation of iodoform and hypoiodous acid by the hydrolysis of carbon tetraiodide is to be accepted without question, the presence of a "positive" iodine in carbon tetraiodide may be accounted for by the following schematic representation:



DISCUSSION OF RESULTS

Before proceeding with the discussion of my study of the hydrolysis of carbon tetraiodide with various reagents, it is necessary to discuss the results of some of my preliminary experiments. First, I have been unable to effect hydrolysis of carbon tetraiodide with aqueous alkali at room temperature. Hydrolysis was negligible when the reaction mixture was boiled for several hours, and allowed to stand for several months. It is quite likely that the insolubility of the carbon tetraiodide in water is responsible for this apparent lack of reactivity. Second, the decomposition of carbon tetraiodide in various solvents is contingent upon the available oxygen. Thus, solutions in methyl and ethyl alcohol decompose quickly (a matter of minutes) if the solutions are shaken while exposed to air. In a sealed tube, and particularly in evacuated tubes, alcoholic solutions of carbon tetraiodide keep fairly well. Little decomposition is noted in the evacuated tubes at the end of three or four days. The stability of carbon tetraiodide is greatest in tertiary butyl alcohol; a sample sealed with air present in the tubes decomposed only after the solution had stood for twenty days at room temperature and for ten hours at 50°. However, a similar experiment with the air removed from the tube did not show any decomposition of the carbon tetraiodide at the end of the heating period. Again, a benzene solution of carbon tetraiodide, when shaken in air, decomposes to give a quantitative yield of iodine within a few minutes, but shows only slight decomposition at the end of six weeks when

⁴ MOISSAN, *Compt. rend.*, **113**, 20 (1890).

kept in an evacuated tube. Similarly, solutions of carbon tetraiodide in chloroform yield iodine readily when in contact with air, but the tetraiodide can be successfully crystallized from this solvent when air is rigidly

TABLE I
HYDROLYSIS OF CARBON TETRAIODIDE AND IODOFORM^d

NO.	IODOMETHANE, MOLES $\times 10^4$		SOL- VENT, CC.	HYDROLYTIC AGENT, MOLES ^a		IODIDE, ^c %	CONDI- TIONS	REAC- TION TIME, DAYS	REMARKS
<i>Experiments in Water</i>									
1	Cl ₄	9.61	5	KOH	1.0	0.0	Air	90	No reaction.
2	CHI ₃	12.7	5	KOH	1.0	0.0	Air	90	
<i>Experiments in Methanol</i>									
3	CHI ₃	5.09	4	KOH	13.0	34.8 V	Air	1	Incomplete; Cl ₄ recovered.
4	CHI ₃	5.09	4	KOH	6.9	58.7 V	Air	2	
5	CHI ₃	5.09	50	KOH	6.9	72.9 V	Air	2	
6	Cl ₄	9.61	50	KOH	6.9	84.7 V	Vac.	1	
7	Cl ₄	9.61	4	KOH	6.9	74.9 V	Vac.	2	
8	Cl ₄	3.85	4	KOH	18.5	67.9 V	Air	1	
9	Cl ₄	9.61	4	KOH	6.9	75.9 V	Air	2	
10	Cl ₄	9.61	5	KOH	5.0	76.0 V	Air	3	
11	CHI ₃	12.7	5	CaO	5.0	0.0 V	Air.	6	
12	CHI ₃	12.7	5	CaO	3.5	0.0 V	Vac.	10	
13	CHI ₃	12.7	5	CaO	4.0	0.0 F	Vac.	30	
14	Cl ₄	5.09	5	CaO	5.0	94.0 V	Air.	6	
15	Cl ₄	5.09	5	CaO	5.0	76.0 V	Vac.	10	
16	Cl ₄	9.61	5	CaO	4.0	81.2 F	Vac.	30	
17	CHI ₃	12.7	5	NaOC ₆ H ₅	4.0	0.0 V	Vac.	2	
18	CHI ₃	12.7	5	NaOC ₆ H ₅	4.0	0.0 V	Air	3	
19	CHI ₃	12.7	5	NaOC ₆ H ₅	4.4	0.0 F	Vac.	30	
20	Cl ₄	9.61	5	NaOC ₆ H ₅	5.0	84.9 V	Vac.	2	
21	Cl ₄	9.61	5	NaOC ₆ H ₅	5.0	84.2 V	Air	3	
22	Cl ₄	9.61	5	NaOC ₆ H ₅	4.6	98.7 F	Vac.	30	

^a Per mole iodomethane.

^b Expressed as percentage of the theoretically possible yield.

^c Initials indicate whether the Volhard or Fajans titration method was used.

^d No free iodine was obtained in any of these experiments.

excluded. This process can be carried out most conveniently in a highly evacuated system.

The results of the hydrolysis experiments upon carbon tetraiodide and

iodoform with a variety of reagents are given in Tables I and II. The hydrolytic experiments with iodoform are of importance from the standpoint of the mechanism suggested by the earlier workers for the hydrolysis of carbon tetraiodide. Iodoform, it may be recalled, is the intermediate product postulated by these investigators in the hydrolysis of carbon tetraiodide. In Table I, experiments 3 to 10 inclusive indicate that potassium hydroxide is not a suitable reagent for the purpose, for it causes the hydrolysis of both iodoform and carbon tetraiodide, and is not the differential reagent needed for the purpose. Calcium oxide and sodium phenolate, however, are ideal hydrolytic reagents. They do not affect iodoform in alcoholic solution (*cf.* experiments 11-13 and 17-19, inclusive), but cause complete hydrolysis of the carbon tetraiodide (*cf.* experiments

TABLE II
EFFECT OF ALKALI AND AIR ON HYDROLYSIS OF CARBON TETRAIODIDE

NO.	CI ₄ , MOLES × 10 ⁴	METHANOL		KOH, MOLES ^a	IODIDE, ^c % ^b	IODINE, % ^b	CONDI- TIONS	REACTION TIME, HOURS	REMARKS
		Conc. ^d	cc.						
1	1.9	60%	5	1	20.8 F	79.2	Air	4	
2	1.9	50%	5	2	58.9 F	41.1	Air	4	
3	1.9	60%	5	3	72.5 F	27.5	Air	4	
4	1.9	60%	5	4	80.7 F	19.3	Air	3	
5	1.9	60%	5	6	98.8 F	0.0	Air	3	
6	1.9	60%	5	1	24.4 F	0.0	Vac.	49	Most of CI ₄ recovered.

^a, ^b, ^c Have the same significance as in Table I.

^d Expressed as percentage of methanol by volume in methanol-water mixture used as solvent.

14-16 and 20-22 inclusive). Another experiment, not listed in the table, in which a mixture of iodoform and carbon tetraiodide was hydrolyzed under similar conditions, showed that the stability of iodoform was not affected by any product from the carbon tetraiodide. These experiments prove beyond reasonable doubt that iodoform is not an intermediate product in the hydrolysis of carbon tetraiodide, and that hypoiodites are not formed in the hydrolysis of this substance.

That my analyses for total iodides are in some cases lower than the calculated values is due in part to incomplete hydrolysis and in part to the use of the Volhard method for the determination of iodides in the reaction mixture. Much better results were obtained by the method of Fajans and Hassel,⁵ and therefore the analytical method is indicated for each experiment in the tables.

⁵ FAJANS AND HASSEL, *Z. Elektrochem.*, **29**, 495 (1923).

Table II shows clearly the effect of air and quantity of potassium hydroxide used on the amount of iodine formed by hydrolysis of carbon tetraiodide. When sufficient alkali is used to neutralize all hydriodic (and carbonic) acid formed, no free iodine is formed. When insufficient alkali is used, iodine is liberated in the presence of air, but not in the absence of air (experiment 6), and in the latter case, hydrolysis is negligible after the alkali is used up. The natural explanation, therefore, is that carbon tetraiodide is attacked directly by the oxygen present in the reaction vessels. Calculations have shown that sufficient oxygen was present to effect this reaction. The decrease in the amount of iodine formed from 79 per cent. to 0 per cent. when the proportion of potassium hydroxide was varied from 1 to 6 moles is very striking, but definitely in accord with the above suggestion.

There remains still one unexplained fact, namely, the formation of iodoform reported by the earlier investigators when the carbon tetraiodide is treated with alkali. My data, as well as my interpretation of the reaction, led me to believe that if the observations of the earlier investigators were correct, the differences in my results are due to the presence of some reducing agents in the solvents used by the earlier investigators. Accordingly, I added small amounts of the corresponding aldehydes to the alcohols used as solvents. Here numerous difficulties were encountered. When insufficient alkali was used, iodine, as expected, was formed, due to oxidation of carbon tetraiodide or intermediate hydrolysis products. With a large amount of alkali and a small amount of aldehyde the normal hydrolysis was faster than the reduction of the carbon tetraiodide to iodoform. The percentage of water in the alcohol is of importance, for water decreases the solubility of the carbon tetraiodide in alcohol. Yet it is possible to choose conditions, even when only minute amounts of the aldehyde are employed, such that substantial conversion of the carbon tetraiodide to iodoform is obtained. Because of the large differences in molecular weight and the small quantities of carbon tetraiodide employed, even a very low concentration of aldehyde in the alcohol would furnish a mole of aldehyde to a mole of carbon tetraiodide. In one experiment with alkali and formaldehyde between 85 per cent. and 100 per cent. of the calculated amount of iodoform was actually isolated. The very large excess of potassium hydroxide was probably unnecessary.

Another phenomenon which may have deceived some earlier investigators, since it temporarily deceived me, is the color change when the dark red carbon tetraiodide is dissolved in an alcohol, with or without alkali, and precipitated immediately with water. The product is a yellow-orange solid, resembling iodoform contaminated with a little carbon tetraiodide much more than it resembles the initial carbon tetraiodide.

I should state further that I am of the opinion that, while the general conclusions drawn concerning Table III are absolutely valid, it will probably be difficult for others to duplicate any given experiment so as to obtain *exactly* the same result as I have recorded. I suspect that such factors as the age and purity of carbon tetraiodide, peroxide content of solvent and aldehyde, alcohol and potassium hydroxide

TABLE III
EFFECT OF ALKALI AND ALDEHYDES ON CARBON TETRAIODIDE^d

NO.	MOLES CHI ₃ × 10 ⁴	ALCOHOL ^e SOLVENT		ALDEHYDE, MOLES ^a	KOH MOLES ^c	REACTION TIME, HOURS	IODIDE, ^c %	IODINE, %	CHI ₃ , % ^b
		Conc.	cc.						
1	1.9	40% Methyl	5	Form-, 1	70	12			94
2	2.0	43% Methyl	7	0	50	7	97.4 F	0.0	0
3	2.0	43% Methyl	7	Form-, 1	50	7	96 F	0.0	0
4	2.0	43% Methyl	7	Form-, 5	50	7	33-46 F	0.0	72-89
5	1.9	50% Methyl	6	Form-, 1	2	3	82.5 F	12.7	0
6	1.9	50% Methyl	6	Form-, 2	2	1.5	58.9 F	41.1	0
7	1.9	50% Methyl	6	Form-, 3	2	5	56.8 F	43.2	0
8	1.9	57% Methyl	7	Form-, 0.1	70	6	98 F	0.0	0
9	1.9	40% Ethyl	5	Form-, 1	1	12	26.3 F	51.5	4
10	1.9	40% Ethyl	5	Form-, 1	70	6	99.4 F	0.0	0
11	1.9	40% Ethyl	5	Acet-, 1	35	1	69.2 F	Remainder a mixture of CHI ₃ and unchanged CI ₄	
12	1.9	40% Ethyl	5	Acet-, 1	70	1	72.3 F		
13	1.9	50% Ethyl	4	Acet-, 1	1	1	29.2 F	62	6
14	1.9	95% Ethyl	4	Acet-, 1	1	0.5	27 F	39.1	33
15	1.9	95% Ethyl	5	Acet-, 1	3	0.17	50.8 F	0.0	47
16	1.9	95% Ethyl	4	Acet-, 2	2	0.25	44.4 F	4.4	59
17	1.9	95% Ethyl	5	Acet-, 3	1	1.5	29.4 F	25.4	20
18	1.9	95% Ethyl	5	Acet-, 3	3	0.17	57.4 F	0.0	32

^{a, b, c} Have the same significance as in Table I.

^d All experiments made on shaking machine in glass-stoppered bottles containing air.

^e Expressed as percentage of alcohol by volume in alcohol-water mixture used as solvent.

concentration, temperature, illumination, and agitation may be very important in determining both reaction rate and products.

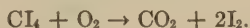
My investigation suggests that the observations of the earlier investigators, that carbon tetraiodide upon treatment with alkali yields iodoform, may be essentially correct. The interpretation of such results, however, is to be sought in the reducing impurities (aldehydes, etc.) which were

most likely present either in the solvents or in the alkali used in the experiments.

EXPERIMENTAL

Preparation and properties of carbon tetraiodide.—Carbon tetraiodide was prepared by the method first suggested by Spindler.⁶ The modifications recommended by Lantenois⁷ were found essential. The carbon tetraiodide prepared by this method could not be successfully crystallized from any organic solvent in air. However, excellent results were obtained by the use of chloroform in a highly evacuated extraction apparatus. I believe that under similar conditions benzene and other low-boiling solvents could be used equally well.

As far as I have been able to find, carbon tetraiodide has not been analyzed successfully, nor have any reproducible physical constants been recorded for that substance. The best analysis for iodine recorded in the literature⁸ is 97.0%, while the calculated value is 97.69%. It can be seen very readily that since the proportion of iodine in iodoform is 96.69%, an iodine analysis does not indicate the purity of carbon tetraiodide. I experienced great difficulty with the analysis of carbon tetraiodide for iodine when the usual methods were employed, such as the decomposition of the sample with sodium in liquid ammonia,⁹ heating with concentrated nitric acid and silver nitrate,¹⁰ etc. However, a rather unusual method of analysis was discovered which gave very satisfactory results. The method depends on an observation, of mine, that when carbon tetraiodide is treated with benzene and the mixture is shaken, iodine is evolved. Presumably the following reaction takes place:



The iodine thus liberated can be titrated with thiosulfate. Actual experiments gave a value for iodine of 97.4% as compared with a theoretical value of 97.69%.

Carbon tetraiodide when crystallized from chloroform (in a highly evacuated system) separates in minute, ruby-red crystals. In view of the fact that oxygen decomposes the substance, it is not at all unusual that the exact temperature of the decomposition of carbon tetraiodide depends on many factors. Thus we have observed that in the light, carbon tetraiodide shows appreciable decomposition in the range 90–100°. On the other hand, when somewhat protected from light practically no decomposition takes place until the temperature reaches 140°. It is thus obvious that one cannot speak of the melting point of the substance. The decomposition point I have observed as 162–165° in a highly evacuated tube protected from light. However, it is possible that this temperature is not perfectly reproducible because of very minute yet significant quantities of oxygen or impurities contained in the system. When pure, carbon tetraiodide keeps fairly well in air in the dark, but decomposes in a few hours in the light. When dissolved in organic solvents in the presence of air, formation of iodine is evident in a few seconds.

Experimental technique.—The solvent or a solution of the hydrolytic agent was placed in a tube, and frozen in a liquid nitrogen bath. Known quantities of carbon

⁶ SPINDLER, *Ann.*, **231**, 264 (1885).

⁷ LANTENOIS, *Compt. rend.*, **156**, 1385 (1913).

⁸ MARK, *Ber.*, **57B**, 1822 (1924).

⁹ VAUGHN AND NIEUWLAND, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

¹⁰ GANE AND WEBSTER, *Z. angew. Chem.*, **22**, 1059 (1909).

tetraiodide (0.1-0.5 g.) were then introduced. In the experiments where calcium oxide was used, the latter was added at this point. The tube was then evacuated thoroughly with the mercury pump and sealed off. Most of the experiments in Tables I and II, made in the presence of air, were conducted by placing the reactants in tubes which were then sealed in air. The experiments of Table III and a few hydrolysis reactions were carried out in glass-stoppered bottles by shaking on a mechanical shaker. All other experiments were carried out in the dark with only occasional agitation. All experiments (except as otherwise noted) were performed at room temperature.

Analysis.—When hydrolysis was complete (as evidenced by the disappearance of solid carbon tetraiodide and its color from solution) the reaction tube was opened, the contents of the tube were either made up to a standard volume for aliquot division, or they were analysed directly. Free iodine was determined by titration with sodium thiosulfate, iodides either by Fajans' method, using sodium eosin as indicator, and *N*/10 silver nitrate, or by the Volhard method. Both determinations were made on the same sample when the Fajans method for iodides was used, the iodine being converted to iodide by thiosulfate and the total iodides then determined. The first titre subtracted from the second gave the iodide content of the original solution. Iodoform was collected on a sintered glass funnel and weighed.

The solubility of iodoform in water (0.01 g. per 100 cc.) and the ease with which iodoform sublimates introduce possible errors of 10% in its determination. It was identified by melting point in several instances.

SUMMARY

1. It has been shown that the instability of carbon tetraiodide in solvents is due to oxygen.
2. It has been shown that hydrolysis of carbon tetraiodide results in the formation of iodide ions, and that no hypoiodites are formed.
3. Reagents have been found which cause the hydrolysis of carbon tetraiodide but are without effect upon iodoform.
4. It has been shown that the formation of iodoform, when carbon tetraiodide is treated in alcohol with alkali, may be accounted for on the basis of the aldehydes present in the alcohol as impurities.
5. There is no factual basis for the assumption that carbon tetraiodide contains positive iodine.

